

Attorney Docket No.: A5031/T433000
AMAT No.: 005031/W&T/WCVD
TTC No.: 016301-043300US

PATENT APPLICATION

HIGH THROUGHPUT PROCESS FOR THE FORMATION OF A REFRACTORY METAL NUCLEATION LAYER

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HIGH THROUGHPUT PROCESS FOR THE FORMATION OF A REFRACTORY METAL NUCLEATION LAYER

BACKGROUND OF THE INVENTION

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1. Field of the Invention

The present invention, in general, relates to semiconductor device manufacturing methods and, in particular, to methods for the formation of refractory metal nucleation layers.

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2. Description of the Related Art

Semiconductor devices (e.g., silicon integrated circuits) often include metal interconnect structures that serve a variety of purposes, including carrying electrical signals between individual device elements, the provision of power, supplying a connection to ground and furnishing a connection to external apparatus. Such interconnect structures include horizontal patterned metal layers separated by intermetal dielectric (IMD) layers formed of, for example, silicon dioxide (SiO_2). The horizontal patterned metal layers are connected by vertical metal interconnects (referred to as vias) formed in the IMD layer.

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One form of conventional via includes a titanium-nitride (TiN) barrier layer and a tungsten (W) core. The tungsten core is normally formed using a tungsten chemical vapor deposition (CVD) reaction. It is difficult to initiate the deposition of a high quality tungsten layer on a TiN barrier layer using tungsten hexafluoride (WF_6) and hydrogen (H_2) gases only, as this approach results in a long "incubation time," i.e., the time between when the gases are introduced to a substrate (e.g., a silicon wafer) and when the deposition is initiated. This approach also results in a tungsten layer with poor thickness uniformity. These problems can be overcome using a CVD reaction that involves reduction of WF_6 with monosilane (SiH_4) to deposit a tungsten nucleation layer on the TiN barrier layer. Tungsten deposition by reduction of WF_6 with SiH_4 has little or no incubation time on a TiN barrier layer, and the resulting layer has minimal thickness nonuniformity. Tungsten is subsequently

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deposited on the tungsten nucleation layer using, for example, the aforementioned tungsten CVD reaction of WF_6 and H_2 .

When tungsten layers are deposited by reduction of WF_6 with SiH_4 , the reaction is typically conducted at a relatively low pressure (e.g., 40 Torr or less) to avoid gas phase nucleation and resultant particle formation. The tungsten deposition rate in this CVD process is determined, among other factors, by the pressure at which the reaction is carried out. By reacting at a relatively low pressure, a low deposition rate is achieved. Since the tungsten nucleation layer is deposited at a relatively low pressure and the tungsten core may be formed at a relatively high pressure (using, for example, the reduction of WF_6 by H_2), process time can be expended cycling and stabilizing between the two deposition pressures. This pressure cycling decreases the effective throughput of the process.

Still needed in the field, therefore, is a high throughput process for forming a refractory metal nucleation layer. In addition, the process should have a high effective throughput.

BRIEF SUMMARY OF THE INVENTION

The present invention provides a process for forming a refractory metal nucleation layer (e.g., a tungsten nucleation layer) with both a high throughput and a high effective throughput. Processes according to the present invention employ a relatively high pressure (i.e., a pressure between 40 Torr and 300 Torr) during formation of the refractory metal nucleation layer. This relatively high pressure facilitates fast wafer temperature stabilization and fast reactions during formation of the refractory metal nucleation layer and, thus, a high throughput process. In addition, the inventive process can be combined with a conventional tungsten deposition technique (e.g., the hydrogen reduction of tungsten hexafluoride to form a tungsten core layer) conducted at a relatively high pressure without the need to expend process time cycling between two different pressures. The use of a relatively high pressure, therefore, enables a high effective throughput process since the pressure cycling required for a subsequent tungsten core layer deposition is eliminated.

5 An embodiment of a method for the formation of a refractory metal nucleation layer (e.g., a tungsten nucleation layer) on a semiconductor device substrate includes first depositing a metallic barrier layer (e.g., a titanium-nitride or tantalum-nitride barrier layer) on the semiconductor device substrate. Next, the metallic barrier layer is exposed to a silicon-
10 containing gas (e.g., a silane gas such as monosilane [SiH₄]) to form a layer of silicon (e.g., a monolayer of silicon) on the metallic barrier layer. The layer of silicon is then exposed to a refractory metal-containing gas (e.g., tungsten hexafluoride, WF₆) such that the refractory metal-containing gas undergoes a reduction reaction with the layer of silicon. The result of this reduction reaction is the formation of a refractory metal layer (e.g., a tungsten metal layer) on the metallic barrier layer. If desired, the silicon-containing gas can be mixed with a nonreactive gas, such as helium or argon, to effectively mix and distribute the silicon-containing gas evenly across the semiconductor device substrate. Subsequently, an alternating exposure of the refractory metal layer to the silicon-containing gas and the refractory metal-containing gas is conducted. This alternating exposure serves to deposit additional refractory metal on the refractory metal layer and thus increase the thickness of the refractory metal layer and form a refractory metal nucleation layer.

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20 By initially forming a layer of silicon on the metallic barrier layer, the uniformity, smoothness and homogeneity of the subsequently formed refractory metal nucleation layer is beneficially improved in comparison to refractory metal nucleation layers formed by conventional processes. Furthermore, by introducing the silicon-containing gas and the refractory metal-containing gas separately, the problem of gas phase nucleation and resultant particle formation at relatively high pressures is eliminated.

25 A better understanding of the features and advantages of the present invention will be obtained by reference to the following detailed description that sets forth illustrative embodiments, in which the principles of the invention are utilized, and the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGs. 1A-1E are simplified cross-sectional diagrams of a substrate as it is subjected to a sequence of steps in a process according to one exemplary embodiment of the 5 present invention; and

FIG. 2 is a flow chart illustrating the process to which the substrate shown in FIGs. 1A-1E is subjected.

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DESCRIPTION OF THE SPECIFIC EMBODIMENTS OF THE INVENTION

To be consistent throughout the present specification and for clear understanding of the present invention, the following definition is hereby provided for a term used therein:

The term “effective throughput” refers to the throughput of a process including all required overhead time (e.g., pressure cycling and temperature stabilization) when the process is operatively combined with another process.

For illustration and exemplary purposes only, the following description of a specific embodiment of the invention pertains to a process for the formation of a tungsten nucleation layer. This specific process includes the use of a titanium-nitride (TiN) barrier layer as a metallic barrier layer, monosilane (SiH₄) as the silicon-containing gas, and tungsten hexafluoride (WF₆) as the refractory metal-containing gas. One skilled in the art will 25 recognize, however, that processes according to the present invention are not limited to the use of a TiN barrier layer, SiH₄ and WF₆ but rather that these serve as representative examples of a metallic barrier layer, a silicon-containing gas and refractory metal-containing gas, respectively.

FIGs. 1A-1E and FIG. 2 are simplified cross-sectional diagrams and a flow chart, respectively, illustrating a sequence of steps in a process for forming a tungsten nucleation layer on a semiconductor device substrate 10 in accordance with an exemplary embodiment of the present invention. A titanium-nitride (TiN) barrier layer 12 is first

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deposited on semiconductor device substrate 10, as shown in FIG. 1A and charted in step 50 of FIG. 2.

TiN barrier layer 12 is referred to as a “barrier” layer since it serves to protect 5 underlying semiconductor device substrate layers (e.g., an underlying titanium [Ti] adhesion layer, not shown) from exposure to, and reaction with, tungsten hexafluoride (WF₆) gas employed in subsequent processing. TiN barrier layer 12 can be formed by conventional techniques, such as the thermal decomposition of a titanium and a nitrogen-containing precursor (e.g., tetrakis-dimethyl-amido-titanium [TDMAT]) or ion metal plasma (IMP) 10 sputtering.

Semiconductor device substrate 10 can be any suitable substrate employed in semiconductor device manufacturing technology. For example, semiconductor device substrate 10 can be a silicon wafer with a metal interconnect structure thereon.

Semiconductor device substrate 10 is depicted in FIG. 1A as including a dielectric layer 14 (e.g., a silicon dioxide [SiO₂] layer or a low-k dielectric layer) overlying a metal layer 16 (e.g., a aluminum layer). Dielectric layer 14 is also depicted in FIG. 1A as having a via opening 18 formed therein.

Next, a layer of silicon (Si) 20 is formed on TiN barrier layer 12 by exposing 20 TiN barrier layer 12 to monosilane (SiH₄, a member of the silane gas family), as illustrated in FIG. 1B (see also step 52 of FIG. 2). TiN barrier layer 12 can be exposed, for example, to SiH₄ under process conditions that result in a silicon surface concentration of 1.5 x 10¹⁵ atoms/cm² (approximately a monolayer of silicon.) It is believed that layer of silicon (Si) 20 takes the form of a H-terminated silicon layer that is distinct from absorbed SiH₄. However, 25 this belief is not intended to limit the present invention.

Suitable process conditions for the formation of layer of silicon 20 include, 30 for example, a semiconductor device substrate temperature in the range of 425 °C to 475 °C, a pressure in the range of 80 Torr to 300 Torr and a SiH₄ flow rate in the range of 50 sccm to 1000 sccm for a time period in the range of 10 seconds to 100 seconds. If desired, the SiH₄ can be diluted in an inert carrier gas such as argon (Ar). Processes for forming a layer of

silicon by SiH₄ decomposition on a TiN layer are further described in U.S. Patent No. 6,303,480 B1 to Desai et al., which is hereby incorporated in full by reference.

Following the exposure of TiN barrier layer 12 to silane, layer of silicon 20 is exposed to tungsten hexafluoride (WF₆, a tungsten source gas). This exposure is conducted such that the WF₆ undergoes a reduction reaction with the layer of silicon, resulting in the formation of a tungsten layer 22 on TiN barrier layer 12. This exposure is charted as step 54 in FIG. 2 and the resulting structure is illustrated in FIG. 1C.

In the circumstance that approximately a monolayer of silicon was formed on TiN barrier layer 12, the appropriate exposure of that monolayer of silicon to WF₆ can result in the formation of approximately a monolayer of tungsten on the surface of TiN barrier layer 12. The combination of a tungsten layer that is a monolayer in thickness on a TiN barrier layer is essentially a tungsten-terminated TiN barrier layer.

Sputtering ion mass spectroscopy (SIMS) depth profiling of a tungsten layer formed in accordance with the present invention indicated that the concentration of silicon incorporated into the tungsten layer was negligible. Therefore, it is postulated without being limiting that the monolayer of silicon is removed as an SiHF₃ byproduct during the formation of the tungsten layer.

Conditions which can be used to form tungsten layer 22 include, for example, a semiconductor device substrate temperature in the range of 375 °C to 475 °C, a pressure in the range of 40.5 Torr to 300 Torr and a WF₆ flow rate in the range of 5 sccm to 30 sccm for a time period in the range of 1 second to 10 seconds. If desired, the WF₆ can be diluted in argon (Ar). For example, 10 sccm of WF₆ can be diluted in 500 sccm of Ar.

An excessive exposure of layer of silicon 20 to WF₆ can result in a deleterious penetration of WF₆ through TiN barrier layer 12. Once apprised of the present disclosure, one skilled in the art will be able to determine acceptable process conditions (e.g., temperature, pressure, time and WF₆ flow rate) that avoid such a penetration while forming tungsten layer 22.

One skilled in the art will recognize that the reduction reaction between WF_6 and the layer of silicon is essentially a surface reaction. This enables the use of a relatively high pressure to provide a relatively fast reaction, and thus a high throughput, while avoiding undesirable gas phase nucleation and the formation of particles. In addition, the use of a

5 relatively high pressure decreases the time required to stabilize at the required process temperature, as a high pressure yields faster heat transfer from the substrate and walls through the gases to the semiconductor device substrate. This serves to further decrease process time and provide a high throughput process for the formation of a tungsten nucleation layer.

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Next, at step 56 of FIG. 2, an alternating exposure of tungsten layer 22 to SiH_4 and WF_6 is conducted to deposit additional tungsten on tungsten layer 22 and, thereby, form tungsten nucleation layer 24 (see FIG. 1D). The phrase “alternating exposure” refers to a process sequence wherein: (a) tungsten layer 22 is exposed to SiH_4 to form a silicon layer on tungsten layer 22; (b) the SiH_4 is purged from a reactor, in which the inventive process is being conducted; (c) the tungsten layer (which has been exposed to SiH_4 and, therefore, has a silicon layer on its surface) is exposed to WF_6 such that the WF_6 is reduced by the silicon layer, thus depositing additional tungsten on tungsten layer 22; (d) the WF_6 is purged from the reactor; and (e) steps (a) through (d) are then repeated as necessary to form a tungsten nucleation layer of a desired thickness.

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The process conditions used during the alternating exposure can be identical to those described above with respect to the exposure of the TiN barrier layer to SiH_4 and the exposure of the layer of silicon to WF_6 . However, it has been determined that the formation of a silicon layer on a tungsten layer takes relatively less time than the formation of a silicon layer on a TiN layer. Therefore, tungsten layer 22 can, for example, be exposed to SiH_4 for as little as 2 seconds.

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Purging of the reactor can be accomplished by stopping the flow of reactive gases (e.g., WF_6 or SiH_4) and continuing or initiating the flow of an inert “carrier” gas, such as argon. The carrier gas flow can be increased during the purging step to decrease the purge time necessary to evacuate the reactive gas. Exemplary purge conditions are 2000 sccm of Ar for 2 seconds.

In the circumstance that the alternating exposure step employs a SiH₄ exposure that forms a silicon monolayer(s), each exposure to WF₆ will deposit an additional monolayer of tungsten on tungsten layer 22. Tungsten nucleation layer 24 can be 20 to 100 angstroms (Å) in thickness. Since a monolayer of tungsten is approximately 3 Å thick, the 5 alternating exposure step can include one to 7 alternating exposures to SiH₄ and WF₆ to deposit a continuous tungsten nucleation film of approximately 20 Å in thickness. A 20 Å thick tungsten nucleation layer can provide as good or better fluorine barrier properties as 100 Å of TiN deposited by MOCVD methods.

10 Next, a tungsten core layer 26 is deposited on tungsten nucleation layer 24 using any of a number of conventional tungsten CVD reactions that are known to those of skill in the art including, for example, those that involve the reduction of WF₆ by H₂ (see FIG. 1E and step 58 of FIG. 2). The deposition of tungsten core layer 26 can be conducted using conventional tungsten CVD reaction conditions. For example, the tungsten CVD reaction can be conducted at a semiconductor device substrate temperature in the range of 375 °C to 475 °C, a pressure in the range of 1 Torr to 300 Torr, a WF₆ flow rate in the range of 1 sccm to 1000 sccm, and an H₂ flow in the range of 10 sccm to 20,000 sccm. If desired, an inert carrier gas, such as argon, can be employed during the deposition of tungsten core layer 26, to more effectively mix and distribute the gases on the wafer.

15 Processes according to the present invention provide several benefits over conventional processes for the formation of a tungsten nucleation layer. First, the process conditions used to form the tungsten nucleation layer can be conducted at a relatively high pressure (i.e., at a pressure in the range of 40 Torr to 300 Torr). This pressure produces a fast 25 deposition rate and thus increases process throughput in comparison to conventional processes for the formation of a tungsten nucleation layer. Furthermore, by avoiding the simultaneous presence of WF₆ and SiH₄ in the process chamber, gas phase nucleation and hence particle formation is avoided even though the process is conducted at a relatively high pressure.

30 Second, the use of a relatively high pressure reduces the amount of time required to reach the desired process temperature since heat transfer is improved at relatively high pressures. This provides a further increase in process throughput compared to conventional processes.

Third, since the pressure employed for formation of the tungsten nucleation layer can be relatively high, tungsten nucleation layer formation processes according to the present invention can be combined with a conventional tungsten CVD reaction (e.g., H₂

5 reduction of WF₆) for the formation of a tungsten core layer at a relatively high deposition rate. By running the inventive process and the conventional tungsten CVD reaction at the same pressure, unnecessary pressure cycling is avoided and a high effective throughput attained.

10 Fourth, by initially forming a layer of silicon on the TiN barrier layer, the smoothness, uniformity and homogeneity of the subsequently formed tungsten nucleation layer is improved compared to conventional tungsten nucleation layer formation processes.

15 The gas flow rates recited and described above are optimized for processes run in a Centura 5200 WxZ chamber manufactured by Applied Materials and outfitted for 200 mm wafers. One skilled in the art will recognize that the rates, at which various precursor gases in the process are introduced, are in part chamber specific and will vary if chambers of other designs and/or volumes are employed.

20 It should be understood that various alternatives to the embodiments of the invention described herein may be employed in practicing the invention. It is intended that the following claims define the scope of the invention and that methods within the scope of these claims and their equivalents be covered thereby.